

## Unoccupied Electronic State of $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ Observed by Inverse-Photoemission Spectroscopy

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The unoccupied electronic state of  $\text{Nb}^{5+}$ -doped  $\text{SrTiO}_3$  ( $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ ) has been studied by inverse-photoemission spectroscopy (IPES). The IPES spectra exhibit three features, which correspond to the  $t_{2g}$ - and  $e_g$ -subbands of the Ti 3d state and Sr 4d state. The peak positions and bandwidths of the IPES spectra are in good agreement with the standard band calculation. The intensity of the  $t_{2g}$ -subband decreases with increasing  $\text{Nb}^{5+}$  concentration. This finding indicates that the doped electron enters the bottom of the Ti 3d-induced conduction band. [DOI: 10.1143/JJAP.43.7623]

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Perovskite-type oxide  $\text{SrTiO}_3$  exhibits  $n$ -type conductivity on substituting  $\text{Nb}^{5+}$  for  $\text{Ti}^{4+}$  and it becomes a superconductor at  $T_c = 0.3$  K. The doped  $\text{SrTiO}_3$  has been extensively used as a substrate for thin film deposition of superconductors and ferroelectrics because of their similar crystal structure and good lattice matching. The photoemission spectroscopy (PES) spectra of  $\text{Nb}^{5+}$ -doped  $\text{SrTiO}_3$  ( $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ ) exhibit two Ti 3d-based features within the band gap region of the parent  $\text{SrTiO}_3$ , which are generally believed to be a coherent part at the Fermi level ( $E_F$ ) and an incoherent part at  $\sim 1.0$  eV from  $E_F$  that is attributed to a remnant of the lower Hubbard band.<sup>1–5</sup> However, the band structure calculation that assumes a rigid-band filling cannot reproduce the  $\sim 1.0$  eV peak, although the shape of the O 2p valence band is in a good agreement with the PES spectra.<sup>1,2</sup> In order to confirm the origin of the 1.0 eV peak, the authors studied the electronic structure of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  using high-resolution X-ray absorption spectroscopy (XAS).<sup>4</sup> Below the O 1s threshold, XAS spectra show two features due to empty states whose energy positions match with those of the two Ti 3d-based features in the band gap energy region observed in the PES spectra. These XAS features exhibit systematic temperature dependence, which is well explained by the Fermi–Dirac distribution function. This result indicates that two Ti 3d features in the band gap are donor states as expected from the rigid-band model.

In this study, the unoccupied electronic state of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  has been measured using inverse-photoemission spectroscopy (IPES). IPES is a powerful technique for investigating an unoccupied electronic state, though the number of experimental IPES studies is a very few.<sup>6–10</sup> Moreover, we show that the band structure of the conduction band of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  also obeys the rigid-band model, as was reported for the valence band side.<sup>3,4</sup>

$\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  samples were prepared by the solid-state reaction of  $\text{SrTiO}_3$ ,  $\text{SrCO}_3$ , and  $\text{Nb}_2\text{O}_5$  at 1200°C for 12 h, and the single crystals were grown by a floating zone method using a Xe arc imaging furnace. The  $\text{Nb}^{5+}$  concentrations were  $x = 0.01, 0.02$  and  $0.05$ . The single crystals were confirmed as being a single phase with a perovskite structure by powder X-ray diffraction analysis.

The IPES measurements were carried out at the Institute for Solid State Physics, University of Tokyo.<sup>7,8</sup> A filament-cathode-type electron gun was used for the excitation source.

The kinetic energy of the electron was calibrated using an electron energy analyzer. The IPES spectra were measured using a soft-X-ray emission spectrometer of Rowland circle geometry that consists of a grating with a groove density of 300 lines/mm and a Cs-coated multichannel detector. The single crystals were scraped *in situ* with a diamond file in a vacuum of  $2.0 \times 10^{-10}$  Torr in order to obtain a clean surface. The measurements were carried out at 25 K. The total resolution was approximately 0.5 eV at the incident electron energy ( $E_k$ ) of 50 eV.

Figure 1(a) shows the IPES spectrum of  $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$  measured at  $E_k = 50$  eV. The abscissa represents the energy above  $E_F$  that was calibrated by the Fermi edge of Au. The determined  $E_F$  is located almost at the bottom of the conduction band, since the sample used in this study has  $n$ -type conductivity. The two prominent features at  $\sim 1.9$  eV and  $\sim 4.0$  eV correspond to the  $t_{2g}$ - and  $e_g$ -subbands of the Ti 3d states, respectively. The energy separation between the  $t_{2g}$ - and  $e_g$ -subbands, which corresponds to the crystal-field splitting, is in accordance with the Ti 2p and O 1s X-ray absorption spectroscopy (XAS) spectra.<sup>4,9</sup>

Figure 1(b) shows the energy band DOS histogram

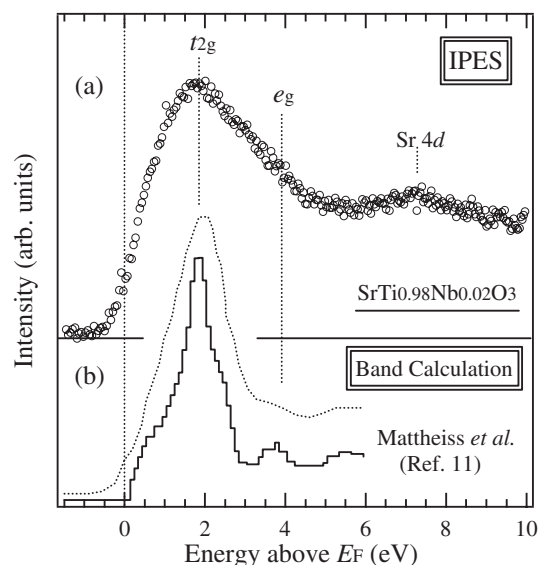


Fig. 1. (a) IPES spectrum of  $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$  measured at  $E_k = 50$  eV. (b) Unoccupied DOS curve calculated by Mattheiss *et al.*<sup>11</sup>

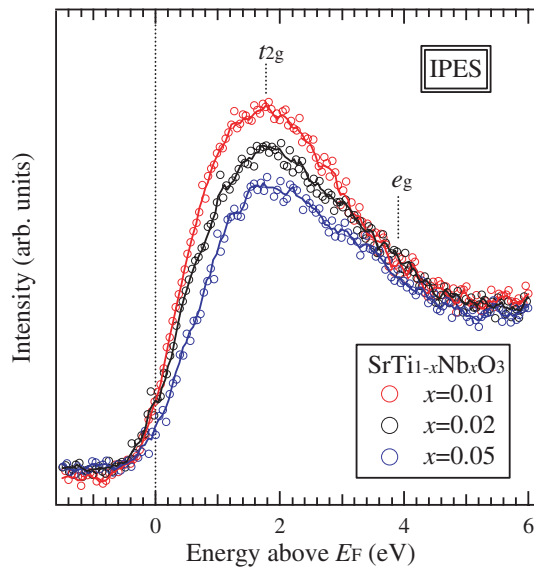


Fig. 2. IPES spectra as function of  $\text{Nb}^{5+}$  concentration of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  measured at  $E_k = 50$  eV. Full line in open circle is obtained by smoothing.

calculated by Mattheiss *et al.*<sup>11)</sup> Mattheiss calculated the DOS histogram using the augmented plane wave (APW) and Slater–Coster linear combination of atomic-orbitals interpolation method. The dashed line shown above the histogram is obtained by convoluting the original DOS with Gaussian broadening functions with widths of 0.5 eV. Compared with the IPES spectrum of Fig. 1(a), the bandwidth and peak positions of  $t_{2g}$ - and  $e_g$ -subbands are in good agreement with the calculated energy band DOS.

Figure 2 shows the IPES spectra as a function of  $\text{Nb}^{5+}$  concentration of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  measured at  $E_k = 50$  eV. The IPES spectra are normalized by measurement time and beam current. The peak positions of the  $t_{2g}$ - and  $e_g$ -subbands do not depend on  $\text{Nb}^{5+}$  concentration. The intensity of the  $e_g$ -subband does not depend on  $\text{Nb}^{5+}$  concentration. The intensity of the  $t_{2g}$ -subband decreases with increasing  $\text{Nb}^{5+}$  concentration, indicating that the doped electrons enter the bottom of the Ti 3d conduction band.

In recent years, the band structure in the conduction band region of the lightly-doped  $\text{SrTiO}_3$  has been calculated by Sarma and co-workers.<sup>6,12)</sup> They used the linear muffin orbital (LMTO) method within the atomic-sphere approximation. From the second-order perturbation applied to the DOS obtained from LMTO supercell calculation, a correlation-induced satellite and surface-induced state appear outside the one-electron bandwidth in the unoccupied states.<sup>6)</sup> This calculation indicates that the band structure of doped  $\text{SrTiO}_3$  does not obey the rigid-band model. However, our results are in good agreement with the one-electron band

calculation, as shown in Fig. 1. The doped electrons enter the bottom of the Ti 3d conduction band and form the impurity state below  $E_F$ . The existence of the impurity state has been investigated in PES and XAS studies.<sup>3,4,9)</sup> Therefore, the above results may indicate that the electronic structure in the conduction band of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  obeys the rigid-band model. On the other hand, the shift of  $E_F$  expected from the rigid-band model is not observed in the present IPES spectra. In the PES study on the same sample, we have already reported that the  $E_F$  shifts to the higher energy side with increasing  $\text{Nb}^{5+}$  concentration.<sup>4)</sup> This shift is smaller than  $\sim 0.1$  eV. We cannot observe the shift of  $E_F$  with Nb doping, since the IPES used in this study had a resolution of 0.5 eV and weak detector coefficients. If the resolution and coefficients of IPES are improved in the future studies, the shift of  $E_F$  might be observed.

In conclusion, we have studied the unoccupied electronic state of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  using IPES. The IPES spectra show two features, which correspond to the  $t_{2g}$ - and  $e_g$ -subbands. The peak positions of the  $t_{2g}$ - and  $e_g$ -subbands are in good agreement with the one-electron band calculation. The intensity of the  $t_{2g}$ -subband of the Ti 3d conduction band decreases with increasing  $\text{Nb}^{5+}$  concentration, indicating that the doped electrons enter the bottom of the empty Ti 3d conduction band. These findings may indicate that the band structure of  $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$  obeys the rigid-band model.

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